

COLLOIDAL PROPERTIES OF BOG WATER

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Introduction

This paper is a report of work on the chemical analysis of bog water, the colloidal state of the material in the water, and the effects of this material on the growth of plants. Much of the work is now reported for the first time, but a brief general statement of some of it has been made in a former paper (13). It is also shown how the data here given tend to explain current agricultural practice in bog utilization.

Sphagnum bogs are very numerous in the Puget Sound region and in Alaska. There is scarcely any portion of western Washington in which they are not found, and in some cases there are continuous areas of approximately 300 acres. The fact that these bogs act as a selective habitat and have a peculiar flora of their own, largely xerophytic, makes them objects of great botanical interest, while the fact that the substratum in them, often to a depth of 30 ft. or more, is composed almost entirely of organic matter, and that they have little or no forest covering, makes the utilization of these areas for agricultural purposes a matter of peculiar economic interest.

The acreage of these bogs now utilized for cranberry culture and for gardens, meadows, and pastures, although considerable, is still very small in comparison with their total area in the region. Every bog is a potential crop-producing area of considerable importance, and whatever we can learn with regard to the fundamental factors that govern the growth of plants in bogs in their natural state may function in their transformation into areas in which food production in this region can be increased.

In former papers the senior author has described the flora of some sphagnum bogs of the Puget Sound region (10) and Alaska (11), and has summarized and discussed the various theories (12) that have been suggested to account for the peculiar character of

the flora present in them and the almost complete inhibition from them of plants other than bog xerophytes. Among the various conditions which are factors in this, the toxic properties of the water have been shown to be very important. He has also (13) published evidence tending to show that the toxic properties of this water are due, at least in part, to the presence of matter in a colloidal state. The present paper gives fuller details of the experimental work pointing to this conclusion. It also reports further experimental evidence tending to support this conclusion and furnishes some evidence as to the colloidal state in which the toxic substances are present.

Experimental work

The samples of bog water used were collected in most cases by digging a hole, usually not more than 30 inches deep, in the substratum, and dipping from this the water that accumulated within a few minutes. When the bogs were too dry to admit of securing water in this way it was squeezed from handfuls of the decaying material. In all cases it was collected in glass containers and taken to the laboratory, where it was strained through washed cheesecloth and then filtered twice through filter paper.

Samples collected from several bogs and filtered in this way were treated with various electrolytes [NaCl , MgSO_4 , $(\text{NH}_2)\text{SO}_4$, and Na_2HPO_4] to determine whether there was any material in the water that could be precipitated by this means.

To a 250 cc. sample from North Mud Lake bog a like volume of saturated solution of $(\text{NH}_2)\text{SO}_4$ was added. After shaking thoroughly this was allowed to stand. At the end of 2 days no precipitate had appeared, but at the end of 5 days a precipitate could readily be seen.

When 90 cc. of water from Fauntleroy bog was saturated with $(\text{NH}_4)_2\text{SO}_4$ by adding the salt gradually and shaking no precipitate appeared at once. When this had stood over night, however, there was a considerable quantity of precipitate, consisting of brown, somewhat flaky particles, some at the surface, some at the bottom, and some remaining suspended in the liquid. This precipitation by complete saturation with $(\text{NH}_4)_2\text{SO}_4$ was repeated

with two samples from the North Mud Lake bog and one sample from each of the following bogs: Maltby bog, Henry bog, and the bogs at Cordova, Alaska, and Sand Point, Alaska. The results in all cases were the same. The work was then repeated by saturating samples from these same bogs with NaCl , MgSO_4 , and Na_2HPO_4 . The results in all cases were the same qualitatively as when $(\text{NH}_4)_2\text{SO}_4$ was used, although the quantity of precipitate varied somewhat. Later precipitation of samples from these bogs and other bogs of the Puget Sound region was tried repeatedly, and in all cases the results were as described.

The precipitate from 7 samples treated with $(\text{NH}_4)_2\text{SO}_4$ was filtered off on filter paper. Each filtrate was then placed in a dialyzing tube of parchment paper and dialyzed in running water until the contents of the tubes showed no precipitate with barium chloride. The toxicity of these filtrates was then tested by growing cuttings of *Tradescantia* in them in the same way that the toxicity of bog water had been tested earlier (10). Controls of *Tradescantia* cuttings in untreated bog water and in Cedar River water were run. The root hairs developed well in the filtrate and in the Cedar River water, while their development was very poor in the bog water. No difference could be seen between those grown in the filtrate and those in the Cedar River water. Samples of bog water were also dialyzed and cuttings of *Tradescantia* were grown in them. They were still just as toxic as untreated samples.

On January 25, 1918, 6 samples of bog water that had been collected from Henry bog on November 5, 1916, and filtered through filter paper on November 7 and again on November 9, 1916, were all found to contain considerable quantities of a brown precipitate in irregular, somewhat flaky, masses. A sample collected from Maltby bog on November 30, 1915, and filtered December 4, 1915, showed the same results, as did also one collected at Sand Point, Alaska in July 1913, and filtered October 27, 1915. A gradual aggregation of the colloidal material occurred with the lapse of time in every case.

In order to test the volatility of the toxic substances, 500 cc. of the filtered bog water was distilled on a water bath until the residue was only 80 cc. The distillate was colorless, while the

concentrate was much darker than bog water. The material in the concentrate all remained in solution. No precipitate appeared and no incrustation was left in the beaker when the concentrate was poured out. The toxicity of the distillate and of the concentrate was tested by growing *Tradescantia* cuttings in samples of them. The concentrate proved to be more toxic than the untreated bog water, while root hairs developed as well in the distillate as they did in Cedar River water. Samples of the concentrate and of the distillate were saturated with solid $(\text{NH}_4)_2\text{SO}_4$ and allowed to stand overnight. The distillate gave no precipitate in any case, while the concentrate gave a much heavier precipitate than did the untreated bog water.

Since all samples of bog water tested had been found acid to litmus and to phenolphthalein, tests of both the concentrate and the distillate were made by titrating with $\text{N}/20\text{NaOH}$, using the same indicators. The acidity of the concentrate was in every case found to be greater than that of untreated bog water. The distillate was slightly acid, but much less so than the untreated water. The precaution of removing the CO_2 by boiling before titrating was taken in each case. Since both the concentrate and the untreated bog water are colored solutions, the use of indicators with them is unsatisfactory, and more exact means would have to be used in order to get quantitative data. Table I summarizes most of these results, together with some presented

TABLE I

Constituents	Precipitate with electr.	Toxicity	Acidity
Bog water	+	+	B
Distillate	—	—	C
Concentrate	+	+	A
Residue	+	+	B

later in the paper. The letters A, B, and C indicate relative acidity, A being greater than B, while C is much less than B.

Work was next undertaken to secure data on the chemical constitution of the materials in solution in the bog waters that had been experimented on and to get some indication as to what

the colloidal state of the toxic material is. Six samples of water were collected for analysis. The usual precautions recommended for the sampling of waters were rigidly followed. The localities were as follows: (1) the swamp adjoining Henry bog, (2) a point approximately in the center of Henry bog some 800 or 900 ft. from the edge of the swamp, (3) a point in West Mud Lake bog about 600 ft. from its edge, (4) another point in the same bog about 500 ft. from where sample 3 was obtained, (5) a very narrow strip of swamp land lying between the points where samples 3 and 4 were obtained, (6) a few inches under the surface of Lake Washington, a short distance from shore, where the water was about 30 ft. deep. These samples are referred to in table II by these numbers.

TABLE II

ANALYSIS OF WATERS FROM SWAMPS, BOGS, AND LAKES

Constituents	1	2	3	4	5	6
Total organic nitrogen.....	2.92	3.09	2.17	2.34	2.31	0.834
Nitrogen as albuminoid ammonia ..	0.855	0.850	1.20	0.526	0.500	0.20
Nitrogen as free ammonia.....	0.52	0.013	0.472	0.420	0.175	0.108
Nitrogen as nitrites.....	0.005	0.003	0.010	0.010	0.012	0.0002
Nitrogen as nitrates.....	0.05	0.05	0.040	0.040	0.030	0.06
Chlorine.....	0.96	1.44	0.708	0.743	0.702	2.70
Oxygen required.....	42.50	41.50	14.50	14.30	16.40	7.55
Total solids.....	109.00	101.20	92.00	93.00	107.00	65.00
Loss on ignition.....	83.50	85.70	62.00	65.00	64.00	20.00

Sample 1 possessed a strong earthy odor and a light straw color. It was collected so close to the edge of the bog as to be considerably influenced by the character of the water of the bog. Sample 2 had a very slight odor, and its color was much deeper than that of sample 1. Samples 3, 4, and 5 all possessed a slight earthy odor and had a light straw color. Sample 6 was perfectly clear and had no odor. Samples 1 and 2 were collected February 20, 1917; samples 3, 4, and 5 were collected March 13, 1917; sample 6 was taken during the spring of 1917. The various constituents of the waters examined were determined according to the methods given in "Standard methods for the examination of water and sewage," used by the American Health Association.

Determinations of the amount of solid matter and of the required oxygen on a few samples of water from other Puget Sound bogs gave results lying within the limits of the values reported for samples 3, 4, and 5. While only one analysis of Lake Washington water is here shown, the junior author has made frequent analyses of lake water in this region and has found them consistent with the analysis here given for Lake Washington water.

In table III the values in column 1 are an average of those in columns 2, 3, and 4 of table II. The values in column 2 are the same as those in column 6 of table II.

TABLE III
COMPARISON OF BOG WATER AND LAKE WATER

Constituents	1 (bog)	2 (lake)
Total organic nitrogen	2.53	0.0834
Nitrogen as albuminoid ammonia....	0.855	0.200
Nitrogen as free ammonia.....	0.301	0.108
Nitrogen as nitrites.....	0.008	0.0002
Nitrogen as nitrates.....	0.043	0.06
Chlorine	0.963	2.70
Oxygen required	23.400	7.55
Total solids	95.400	65.00
Loss on ignition.....	70.900	20.00

FOULK (7) has made two analyses of Ohio bog water. A period of two years elapsed between the time of taking the two samples, which were from the same bog. The two analyses differ considerably, but both agree with the ones here reported in showing a large oxygen requirement and a large loss on ignition.

Several samples of Puget Sound bog water were evaporated to dryness in porcelain dishes on a water bath. A dark brown powdery residue was obtained. Other samples were evaporated to dryness in a porcelain dish heated over a Bunsen burner and protected only by a thin piece of asbestos and wire gauze. The residue so obtained was of the same appearance as that from the water bath evaporation. Some of the residue from the water bath evaporation was heated to redness in a porcelain dish. It gave no protein odor as it burned. The biuret test for protein

was applied to other portions of this residue. The results were negative in every case. The solubility of this residue was then tried. It dissolved readily in cold Cedar River water. Solution was complete in a volume of Cedar River water equal to the volume of bog water from which the solid matter was obtained. The toxicity of this solution of solids in Cedar River water was tested by growing cuttings of *Tradescantia* in it, with other cuttings in bog water and Cedar River water as controls. The bog water and the solution of bog solids greatly reduced root hair development on the cuttings, while root hairs developed abundantly on cuttings in Cedar River water. The water solution of this residue was found to reduce Fehling's solution slightly.

The brownish residue was found to be insoluble in alcohol and gasoline. In all cases but one it was also found entirely insoluble in ether. In this one case enough went into solution to impart a brownish color to the porcelain dish in which the ether was allowed to evaporate. When bog water was shaken with an equal volume of ether in a separatory funnel nothing was extracted from it.

An attempt was made to throw out the solid matter in bog water by centrifuging it. Samples were centrifuged for 20 minutes at 1800 revolutions, but no solid matter at all was thrown out.

Discussion

The experimental data furnish evidence as to the substances present in the water of sphagnum bogs, and also certain indications in regard to the colloidal state of the soil solution in them and the relation of this colloidal material to the toxicity of the water. They have also a considerable bearing on agricultural utilization of these areas.

The large amount of organic matter in bog water as compared with lake water is clearly shown by the large amount of solid matter and the loss sustained when this solid matter is heated to full redness. The solid matter in bog water is 146 per cent of that in lake water. The solid matter from bog water lost 74 per cent of its weight on ignition, while that from lake water lost only 30 per cent. That this organic matter is still in a very limited state of oxidation is indicated by the large amount of oxygen that

is required. More than three times as much oxygen was required by the bog water as by lake water.

The large amount of solid organic matter in bog water is evidently the result to a large extent of the breaking down of plant tissues in the absence of an adequate supply of oxygen. The interstices of the decaying mass of material are full of water at all times at a depth of 2 ft. or more, and even in the first 2 ft. except occasionally for a brief time in midsummer. Since organisms are abundant in bogs, it seems evident that the nature of the products must be conditioned by at least 3 factors: (1) the original composition of the decaying materials, (2) the organisms present, (3) the environmental conditions under which they act. DACHNOWSKI (5, 6) has emphasized the reducing power of bog soils, and has found that aeration lowers the toxicity of the water to agricultural plants. KLEIN (9) had made suggestions along this line as early as 1880.

A very large amount of the nitrogen present in bog water is in the organic form. The total organic nitrogen content of the bog water here reported is over three times as much as that of the lake water reported. In the bog water the total organic nitrogen is 50 times the combined nitrite and nitrate content, while in the lake water it is only 14 times.

The work of JODIDI (8) and of ROBINSON (16) show large amounts of nitrogenous matter in bog soils, and indicate that it is either already in the form of amino acids and acid amides, or is capable of being converted readily into these compounds.

The amount of nitrogen as nitrates is slightly larger in the lake water than in the bog water. Even if this difference were large it could not be accepted as necessarily indicating a difference between the nutritive value of the two waters for plants, since it is well known that some organic compounds are beneficial to plant growth (2, 4, 17, 19). A number of these beneficial organic compounds are nitrogenous. BOTTOMLEY'S (2) work indicates the abundance of such a compound in sphagnum peat that has been acted upon by aerobic soil organisms.

The amount of nitrogen as free and albuminoid ammonia varies considerably in the different analyses, and the existence of

nitrogen in these conditions is apparently influenced to a large extent by immediate local conditions.

KLEIN (9) was the first one to suggest that the toxicity of bog water is due to the presence of chemical combinations harmful to plant life. The water from a black bog overflowed into the meadows of a certain portion of East Prussia, causing considerable damage. He analyzed this water and found 312.8 parts per million of organic matter and 175.9 parts per million of inorganic matter. Among the reasons which he points out as to why this water is injurious to crop production these two are of special interest: (1) it acts as a reducing agent, (2) it produces chemical compounds that are harmful to plant life. The bog he studied differed from Puget Sound bogs in having considerable mineral content. Our bogs and his have in common the avidity of the organic matter for oxygen. His suggestion of toxicity is the earliest one seen by the authors. The review of his work says that when exposed to air the moist peat soon took up oxygen, with the result that there was formed on the surface of the soil a hard crust which was "impervious to the oxygen of the air, and the humus, withdrawing oxygen from the iron compounds, formed salts destructive to vegetable life." It does not seem positive from this wording whether the "salts destructive to vegetable life" came from the iron compounds or from the humus.

Previously published results (15) indicating that the osmotic pressure of bog water is very low had suggested that the material in solution in it is probably in a colloidal state. The data given seem to confirm this view, while the experiments with *Tradescantia* cuttings indicate that the matter in the colloidal state is a large factor in the toxicity of the water.

BAUMAN and GULLY (1) have shown that the acidity of bog water is due to the colloidal material of the cell walls of the hyaline cells of sphagnum. This would seem to suggest that both the acidity and the colloidal properties of bog water are due to the breaking down of sphagnum. The senior author has suggested in an earlier paper (10) that since the essential conditions for the formation of a bog are the continued growth of sphagnum and the

lack of drainage, the place to look for the origin of the toxicity is in the decay of sphagnum under anaerobic conditions. It seems probable (but is not proved) that the acidity, the colloidality, and toxicity all have their origin here.

It seems clear that the substances in bog water that are precipitated by electrolytes and on long standing without electrolytes, and will not dialyze through parchment paper, and, although present in considerable quantities, do not appreciably lower the freezing point of the water, are in a colloidal state. Since bog water and preparations from it (for example, the concentrate and the solution of the residue from evaporation) which contain these substances are toxic to *Tradescantia* cuttings, while preparations that do not contain them (the distillate) are not toxic, it appears that the toxicity is associated with the matter that is in a colloidal state. Concerning the nature of the colloid we have the following indications.

1. The colloid is thermo-stable. This is indicated by the fact that the distillate is non-toxic, while the concentrate is more toxic than untreated bog water.

2. The colloid is reversible, because when obtained as solid matter it is quickly redissolved on the addition of a volume of cold water equal to the volume of bog water from which the solid was originally obtained.

3. The solid material of bog water when obtained in the dry form is a granular powder. Since the distillate from which this was obtained as a residue is not colloidal, and since a solution having colloidal properties can be obtained by redissolving this solid matter, it seems that it is the material that is in the colloidal state.

4. Bog water has elsewhere (15) been shown to have a slightly lower surface tension than that of pure water. To what extent this may be due to the presence of the colloid has not been determined.

5. No means has been found of testing the swelling of this colloid, since it goes into solution so readily.

6. No evidence has been found that the colloids increase the viscosity of the water.

One means used in the Puget Sound region for bringing these bogs into cultivation is to drain them, scalp off and remove the living vegetation at the surface to a depth of 8 or 10 inches, and then stir up and aerate the partially decayed matter underneath. It seems probable that the success of this plan finds its explanation largely in the removal of much of the toxic material in draining off the water, and the oxidation of the remainder to non-toxic compounds when the soil is exposed to the air.

The work of BOTTOMLEY indicates that a substance or substances beneficial to the growth of higher plants and also increasing the rate of nitrogen fixation by soil organisms results from the action of aerobic soil organisms on sphagnum peat. To what extent the beneficial effects of the aeration of bog soils may be due to oxidation independent of organisms, and to what extent it may be due to the action of organisms under the changed conditions, have not been determined. It seems likely that crop plants in bogs that have been brought into cultivation are influenced beneficially by these compounds. To what extent this beneficial effect may result from actual use of these compounds as definite constituents of plant foods, or to what extent it may be due to their general catalytic effects or their part in certain definite types of metabolism, is not known. SCHROEDER (18) found that the direct application of peat alone to sandy soils gave increased yield of crops, although still better results were obtained when lime and stable drainings were used with the peat. Another practice for bringing these bogs into cultivation is that of destroying the surface vegetation by fire during the dry season. Usually the fire does not penetrate far into the sphagnum substratum because of the moisture beneath.

This practice results, of course, in the practically complete oxidation of the material in the surface layer of the bog. The preparation of the burned-over bog for the planting of crops and the subsequent cultivation of these crops secure aeration and consequent oxidation of the unburned material and also render the soil lighter by mixing the ashes with it. The acidity of the soil is neutralized to a considerable extent by the basic properties of the ash when it goes into solution.

In the main, however, the success that has been attained in the cultivation of bog lands in the Puget Sound region has been attained by the use of acid-tolerant crops (3) such as cranberries, strawberries, celery, onions, lettuce, cabbage, and carrots, rather than by correcting the acidity in order to grow crops that are not acid tolerant.

Summary

1. Bog water gives a precipitate on standing a few hours after saturation with electrolytes.

2. It also gives a precipitate on standing a year or more without electrolytes.

3. The filtrate from the precipitation with $(\text{NH}_4)_2\text{SO}_4$, when dialyzed until free from sulphates, is not toxic to the root hairs of *Tradescantia* cuttings.

4. Bog water, when dialyzed for the same length of time as this filtrate, is toxic to these root hairs.

5. The distillate from bog water gives no precipitate with electrolytes, is much less acid than bog water, and is not toxic to these root hairs.

6. The concentrate obtained when bog water is distilled to approximately one-sixth of its original volume gives a heavier precipitate with electrolytes than does bog water. It is also more acid and more toxic to these root hairs.

7. The residue from complete evaporation of bog water is a brownish powder which is soluble in cold water, insoluble in alcohol and gasoline, and practically insoluble in ether.

8. This water solution of the residue is toxic to the root hairs of *Tradescantia*.

9. No solid matter was thrown out of bog water by centrifuging.

10. Chemical analyses of Puget Sound bog waters give results similar to those reported for other American bog waters.

11. The toxicity of bog water to *Tradescantia* cuttings seems to be connected with the matter in it that is in a colloidal state.

12. The oxidation of this toxic matter to non-toxic matter seems to be a basis of agricultural practice in bringing bog lands into cultivation.

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